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Quarterly Progress Report

Division 8

Solid State

15 July 1964

Prepared under Electronic Systems Division Contract AF 19(628)-500 by

Lincoln Laboratory

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Lexington, Massachusetts



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Quarterly Progress Report

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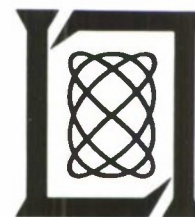
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Lincoln Laboratory

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Lexington, Massachusetts



INTRODUCTION

This abbreviated report covers the work of Division 8 from 1 April 1964 through 30 June 1964. A more detailed presentation is covered by the Solid State Research Report for the same period.

15 July 1964

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REPORTS BY AUTHORS IN DIVISION 8

15 April through 15 July 1964

PUBLISHED REPORTS

Journal Articles*

JA No.

2253A	The Nernst-Ettingshausen Energy Conversion Figure of Merit for Bi and Bi-4% Sb Alloys	T. C. Harman J. M. Honig S. Fischler	Solid-State Electronics <u>7</u> , 505 (1964)
2265	Superconductivity in the High-Pressure InSb-Beta-Sn System	S. D. Nye M. D. Banus H. C. Gatos	J. Appl. Phys. <u>35</u> , 1361 (1964)
2268	Galvanomagnetic Effects in n-Type Germanium	W. E. Krag M. C. Brown	Phys. Rev. <u>134</u> , A779 (1964)
2270	Partial Pressures in Equilibrium with Group IV Tellurides. I. Optical Absorption Method and Results for PbTe	R. F. Brebrick A. J. Strauss	J. Chem. Phys. <u>40</u> , 3230 (1964)
2285	Partial Pressures in Equilibrium with Group IV Tellurides. II. Tin Telluride	R. F. Brebrick A. J. Strauss	J. Chem. Phys. <u>41</u> , 197 (1964)
2293	Growing Helical Density Waves in Semiconductor Plasmas	C. E. Hurwitz A. L. McWhorter	Phys. Rev. <u>134</u> , A1033 (1964)
2296	Growth of $(\text{Ga}_x\text{In}_{1-x})\text{As}$ Single Crystals by Vapor Phase Reaction	R. C. Serrine†	J. Electrochem. Soc. <u>111</u> , 750 (1964)
2303	2000-A Pulse Generator	N. A. Sullivan	Rev. Sci. Instr. <u>35</u> , 639 (1964)
2307	Impurity States in Semiconducting Masers	H. J. Zeiger	J. Appl. Phys. <u>35</u> , 1657 (1964)
2372	Lattice Energy Transfer and Stimulated Emission from $\text{CeF}_3:\text{Nd}^{+3}$	J. R. O'Connor W. A. Hargreaves†	Appl. Phys. Letters <u>4</u> , 208 (1964)
MS-881	AC Susceptibility Measurements on Transition Metal Superconductors Containing Rare Earth and Ferromagnetic Metal Solutes	M. Strongin‡ E. Maxwell‡ T. B. Reed	Rev. Modern Phys. <u>36</u> , 164 (1964)

* Reprints available.

† Author not at Lincoln Laboratory.

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UNPUBLISHED REPORTS

Journal Articles

JA No.

2305	Diffused Junction Diodes of PbSe and PbTe	J. F. Butler	Accepted by J. Electrochem. Soc.
2332	Partial Pressures in Equilibrium with Group IV Tellurides. III. Germanium Telluride	R. F. Brebrick	Accepted by J. Chem. Phys.
2335	Band Edge Structure of PbS, PbSe, and PbTe	J. O. Dimmock G. B. Wright	Accepted by Phys. Rev.
2344	Galvano-Thermomagnetic Effects in Semiconductors and Semimetals. IV. Mercury Selenide	T. C. Harman	Accepted by J. Phys. Chem. Solids
2366	Spontaneous Bending of Thin {111} Crystals of III-IV Compounds	M. C. Finn H. C. Gatos	Accepted by Surface Science
2370	Theory of Electromagnetic Field Measurement and Photoelectron Counting	P. L. Kelley W. H. Kleiner	Accepted by Phys. Rev.
2376	Cyclotron Resonance: (Diamagnetic Resonance)	G. F. Dresselhaus	Accepted by <u>Encyclopedia of Physics</u>
2379	The Pulsed Laser Dosimeter: An Optical Safety Monitor	J. J. Schlickman R. H. Kingston	Accepted by Electronics
2383	Partial Pressures and Gibbs Free Energy of Formation for Congruently Subliming CdTe(c)	R. F. Brebrick A. J. Strauss	Accepted by J. Phys. Chem. Solids
2388	Lasers	R. H. Kingston	Accepted by <u>Encyclopedia of Physics</u>
2398	Temperature Dependence of Attenuation of 70 Gcps Acoustic Waves in Quartz	J. B. Thaxter P. E. Tannenwald	Accepted by Appl. Phys. Letters
2399	Galvano-Thermomagnetic Phenomena and the Figure of Merit in Bismuth. I. Transport Properties of Intrinsic Material	T. C. Harman J. M. Honig B. M. Tarmy	Accepted by Advanced Energy Conversion
2405	PbTe Diode Laser	J. F. Butler A. R. Calawa R. J. Phelan, Jr. T. C. Harman A. J. Strauss R. H. Rediker	Accepted by Appl. Phys. Letters
2410	Diamagnetism	J. B. Goodenough	Accepted by <u>Encyclopedia of Physics</u>

Unpublished Reports (Continued)

Meeting Speeches*

MS No.

797A	Growing Helical Density Waves in Semiconductor Plasmas	C. E. Hurwitz	Symposium, Boeing Aircraft Company, Seattle, Washington, 29 June 1964
983A	Stoichiometry of Electronic Materials	A. J. Strauss	Colloquium, Texas Instruments, Inc. Dallas, Texas, 11 June 1964
985A	Experiments on Room Temperature Nernst-Ettingshausen Refrigerators	T. C. Harman J. M. Honig S. Fischler A. E. Paladino	SAE-ASME National Aeronautic and Space Meeting, New York, 27-30 April 1964
989	Concerning the Existence of Subsequioxides of Praseodymium	D. S. Chapin J. M. Honig	Fourth Rare Earth Conference, Phoenix, Arizona, 22-25 April 1964
1001A	Band Edge Structure of PbS, PbSe, and PbTe	J. O. Dimmock G. B. Wright	Seminar, U. S. Naval Ordnance Laboratory, Silver Spring, Maryland, 16 April 1964
1006	Phonon Generation at 70 kMcps	J. B. Thaxter P. E. Tannenwald	PTGMTT International Symposium, New York, 19-21 May 1964
1006A	Generation of Ultrasonic Phonons in Quartz at 70 kMcps	J. B. Thaxter	Physics Seminar, University of Maine, 13 May 1964
1024A	Stimulated Raman Scattering	H. J. Zeiger	Colloquium, Lowell Technological Institute, 6 May 1964
1032	Photographic Emulsions as Ion Detectors in Quantitative Mass Spectrography	E. B. Owens	ASTM Committee E-14 Symposium on Techniques of Solids, McGill University, 10 June 1964
1036	Magnetoreflexion Experiments in Pyrolytic Graphite	M. S. Dresselhaus	Seminar, Purdue University, 9 April 1964; Seminar, M.I.T. 14 April 1964; Seminar, Ohio State University, 2 June 1964
1061	Thermal Plasmas: Part I. Calculation of Equilibrium Plasma Properties Using Linear Plasma Thermodynamics	T. B. Reed	American Physical Society, Washington, D. C., 27-30 April 1964
1062	Thermal Plasmas: Part II. Plasma Flame Temperature Measurement Using Aureole Isotherms	T. B. Reed	

* Titles of Meeting Speeches are listed for information only. No copies are available for distribution.

Unpublished Meeting Speeches (Continued)

MS No.

1093A	Stimulated Raman Processes	H.J. Zeiger	General Telephone and Electronics Laboratories, Bayside, New York, 28 May 1964
1096	Interface-Alloy Epitaxial Heterojunctions	R.H. Rediker S. Stopek J.H.R. Ward	The Electrochemical Society, Toronto, Canada, 3-7 May 1964
1104	Syllabus Pertaining to Physical Adsorption of Gases on Solids	J.M. Honig	Summer Conference Lecture, University of Michigan, 25-27 May 1964
1110	Principles of Injection Lasers	R.H. Rediker	IEEE Computer Elements Subcommittee, Atlantic City, New Jersey, 16-17 April 1964
1116	Transition-Metal Oxides with Metallic Conductivity	J.B. Goodenough	Conference on the Structure and Properties of Dielectric Materials, M.I.T., 16-17 June 1964
1119	Injection Lasers	I. Melngailis	Seminar, Carnegie Institute of Technology, 16 April 1964
1121	Optical Maser Spectra Deduced from Photoelectron Counting	C. Freed H.A. Haus*	Twenty-Second Annual Conference on Electron Device Research, Cornell University, 24-26 June 1964
1125	Electrochemical Demer Effect in Semiconductor	W.W. Harvey M.C. Finn	International Conference on Physics and Chemistry of Solid Surfaces, Brown University, 21-26 June 1964
1127	Galvano-Thermomagnetic Effects in Semiconductors and Semimetals. IV. Mercury Selenide	T.C. Harman	Seminar, M.I.T., 8 May 1964
1130	Transfer Characteristics and Spectral Response Measurements on Infrared	R.R. Billups L.D. Miller*	IRIS Specialty Group Meeting, Santa Barbara, California, 16 June 1964
1136	Gunn Effect in GaAs	A.G. Foyt A.L. McWhorter	IEEE 1964 Solid State Device Research Conference, Boulder, Colorado, 1-3 July 1964
1137	Properties of InAs-GaSb Interface-Alloy Junctions	E.D. Hinkley R.H. Rediker	
1148	Injection Luminescence in PbTe Diodes	J.F. Butler A.R. Calawa R.J. Phelan, Jr. T.C. Harman A.J. Strauss R.H. Rediker	

* Author not at Lincoln Laboratory.

Unpublished Meeting Speeches (Continued)

MS No.

1142	Magnetoreflexion Experiments in Antimony	M. S. Dresselhaus	Seminar, National Magnet Laboratory, M.I.T., 23 June 1964
1147	Valence-Bond-Molecular Orbital Study of an Hexagonal Ring of Hydrogen Atoms	E. G. Larson W. R. Thorson*	Symposium on Molecular Spectroscopy, Ohio State University, 15 June 1964

* Author not at Lincoln Laboratory.

I. SOLID STATE DEVICE RESEARCH

Laser action has been observed at 12°K in diodes of PbTe which had been prepared by diffusing lead into appropriately annealed p-type material. The emitted coherent radiation was at 6.5 microns as compared to 5.2 microns from InSb diodes, the longest wavelength semiconductor laser previously reported. For a diode with a cavity length of 0.62 mm, mode structure has been observed in the spectrum of the output radiation with a spacing between maxima of 67 Å; this should be compared to a value of 59 Å calculated using the room-temperature value of 5.75 for the refractive index and neglecting the dispersion term. The width of the individual modes is less than the 20-Å resolution of the spectrometer used. Lead telluride, a IV-VI compound, is a direct-gap semiconductor and has its band extrema at the edge of the Brillouin zone in the $\langle 111 \rangle$ direction (L-point), rather than at $k = 0$ as in the III-V laser compounds. Thus, in addition to extending the wavelength range of semiconductor lasers to 6.5 microns, we have demonstrated that laser action is not restricted to III-V compounds and may be associated with direct transitions other than those at $k = 0$. The range of semiconductor materials in which laser action should be possible has been further expanded.

Interface-alloy junctions between InAs and GaSb have been studied. In particular, results have been obtained for junctions formed between an A {111} face of n-GaSb and a B {111} face of p-InAs under an inert gas pressure of 80 atmospheres. Visual microscopic inspection and electron beam microprobing indicate that the junction itself is single crystal and the transition region is approximately 5 microns wide. The heterojunctions when forward biased emit considerable radiation at 0.4 eV (the forbidden energy gap of InAs) and a very much smaller amount of radiation at 0.8 eV (the forbidden energy gap of GaSb). The GaSb acts as a transparent substrate for the 0.4-eV radiation. The photovoltaic response of these heterojunctions has been investigated as a function of the energy of the incident photons. A small relatively constant response is seen for photon energies between that of the two bandgaps and an abrupt increase in photovoltage is observed as the photon energy reaches the bandgap of GaSb. These electro-optical results suggest a band model in which there is a barrier in the conduction band at the heterojunction interface. Such a barrier could be produced by a plane of dislocations in a graded heterojunction and is also predicted by the Anderson model for an abrupt heterojunction, in which case the barrier is caused by the bandgap discontinuity.

In the vapor growth of $(\text{Ga}_x\text{In}_{1-x})\text{As}$ single crystals, it has been found that 2.75 atomic percent indium produces material that lases at 77°K at a wavelength of 8700 Å which is quite close to the pumping band of the Nd^{+3} paramagnetic ion laser. Work is in progress to grow high-quality crystals of this mixture and decrease the threshold current density from its present value at 77°K of 10,000 amp/cm².

The spectrum of the instability in the current through samples of n-GaAs at high electric fields – the Gunn effect – is affected by the value of impedance used to terminate the sample.

For high termination impedance the spectrum is very broad. As the impedance is lowered, a narrow peak begins to appear in the spectrum at $f = v_d/L$ and also at $f = 2v_d/L$. As the impedance is further lowered, the power in the broad-band noise decreases and the peak at $f = v_d/L$ increases in amplitude with a bandwidth that is apparently limited by the length of the voltage pulse applied to the sample. Magnetic effects on the instability have been more carefully investigated. Neither longitudinal nor transverse magnetic fields have any effect on the threshold. Above threshold, the amplitude of the instability is reduced considerably by a transverse field, and to a lesser extent by a longitudinal field, with the longitudinal effect possibly due to misorientation of the sample. The critical electron drift velocity corresponding to the threshold is higher at 77° than at 300°K, contrary to what might be expected for most plasma effects in which there is competition between drift and thermal velocities.

II. LASER RESEARCH

Stimulated Raman emission in nitrobenzene at 90° to the ruby laser beam has been obtained. This is the first step toward constructing a Raman laser which is pumped by an array of ruby lasers at 90° to the Stokes beam and provides further support for certain theoretical models of the Raman laser action. The previously described cylindrical focusing of the ruby beam into a Fabry-Perot cavity was used.[†] Spectral analysis of the 90° Stokes emission indicates that more than four axial modes and a continuum of transverse (or walk-off) modes are oscillating in the Raman cavity. The beam divergence is about 2 mrad, the amount expected for the small cavity that was used. There are strong indications that a stimulated Brillouin-shifted Stokes emission exists at 90°. Estimates of the single-pass gain at 90° are close to previous estimates of the gain at 0°.

Stimulated Raman emission in bromoform occurs in a wide spectrum of combination Stokes and anti-Stokes lines. The data on frequency shifts and emission angles agree with calculations.

Laser properties of grown single crystals of CeF_3 and the transfer of lattice energy which leads to stimulated emission from $CeF_3:Nd^{+3}$ have been investigated. CeF_3 is an interesting laser host because of a direct energy transfer from the lattice to the rare-earth ion, radiative energy transfer due to the intense fluorescence ($d \rightarrow f$) of Ce^{+3} , and the rapid depopulation of the terminal laser state within the $F_{7/2}$ lattice absorption. This absorption can also be used to modulate the laser output.

Laser-created gaseous breakdown of air and argon has been studied by means of emission spectra, frame and streak photographs, and magnetic field and pressure effects. The spark temperature is estimated from the spectral continuum to be about 7000°K. The luminous front of the spark grows parallel to the laser beam at about 5×10^5 cm/sec. A DC magnetic field of about 100 kgauss produced no reduction of the breakdown electric field, in agreement with theoretical estimates that diffusion and hence magnetic field effects are negligible. The measured

[†] Solid State Research Report (1964:1), p. 19, DDC 601830.

breakdown threshold in argon as a function of pressure (between 20 and 2000 psi) agrees with that observed by Meyerand and Haught.

A pulsed laser dosimeter has been developed to warn of dangerously high laser energy being reflected from surfaces into the eye. The instrument consists of a commercially available gamma-ray detector, used as an electrometer, which is connected in parallel with a phototube. When the dosimeter is held to the eye and is pointed at the illuminated surface, the meter reads according to the amount of photocurrent produced by the incident laser light. The safety level was set by clinical data on the critical energy density for retinal damage by spiking ruby lasers with total pulse widths of 175 μ sec.

Experimental results have been obtained on the statistics of the photoelectron counts of photomultipliers illuminated by laser light at 6328 Å, both above and below oscillation threshold. These results indicate that the mean-square fluctuations of a laser oscillating in a single mode are those of a Poisson distribution, while the fluctuations of the noise below oscillation threshold are those of a few narrow-band Gaussian-distributed oscillators. The experimental curves for the mean-square fluctuations as functions of the observation time have yielded estimates for the depth of modulation of the laser output.

Laser oscillation at 2.02 microns in pure xenon has been observed in a 20-cm triode gas laser tube. A gain of 50 percent per meter was measured. The triode structure provides an approximately mono-energetic electron current which should produce population inversion more efficiently than a discharge current. Feasibility of a crossed electron and atom beam high-gain laser experiment is being determined by how low an atom density will still sustain oscillation.

Experiments in which attempts have been made to produce laser oscillation in a mercury-molecule vapor system show promise of output powers at about 5000 Å in the kilowatt range. It is believed that the rapid emptying of the lower state by dissociation yields population inversion during pulsed operation at nearly atmospheric pressure. Power saturation, it is estimated, would occur at about 1-Mw output power.

III. MATERIALS RESEARCH

It has been found that the power output of an RF generator can be conveniently measured by determining the equilibrium temperature of a black-body load with an optical pyrometer and by using the black-body formula to obtain the power radiated by the load. Graphite is an excellent dummy load for studying the output of generators to such relatively high-resistivity loads as plasmas and semiconductors. The pyrometer method has been used to determine the coupling efficiency of a generator as a function of the ratio of load diameter to coil diameter.

Analysis of crystal growth from the vapor shows that constitutional supercooling, which results in instability of the growth interface, can occur in the gas phase as well as in a melt. The analysis yields an expression for the maximum rate of growth from the vapor (v_{\max}) which is possible without constitutional supercooling. Evidence for constitutional supercooling has been obtained in experiments on the growth of iodine by forced convection. At sufficiently low

growth rates the interface is smooth, but it becomes rough when the growth rate exceeds a value close to the calculated value of v_{\max} .

The temperature dependence of the Seebeck coefficient and resistivity have been measured for polycrystalline samples of CrO_2 and CrO_{2+y} , and for single crystals of Cr_2O_3 and MnO . A molecular orbital energy diagram is proposed for CrO_2 which accounts for the ferromagnetism and metallic conductivity of this compound. An energy diagram is also proposed for Cr_2O_3 . According to this diagram, Cr_2O_3 is expected to be a semiconductor with hopping-electron conductivity. The observed electrical properties are consistent with this prediction.

The heat of transformation for the α - β transition in Ag_2Se has been calculated by application of the thermodynamic relation $(dT/dP) = T\Delta V/\Delta H$ to previous data for the pressure dependence of the transition temperature. The value obtained is 2.56 kcal/mole, which is in fairly good agreement with the value of 2.19 kcal/mole measured with a differential scanning calorimeter.

The temperature dependence of the rate at which cubic $\text{PrO}_{1.5}$ is transformed into the stable hexagonal form has been investigated by annealing carefully dried samples of the cubic phase in a high-temperature x-ray diffraction camera. The results are consistent with previous data, obtained by x-ray diffraction measurements at room temperature of samples that had been annealed and then quenched, which show that in the range 800° to 850°C the transformation rate rapidly increases to high values.

The high-pressure tetragonal phase of InSb (InSb_{II}) and solid solutions of InSb_{II} -Sn prepared at high pressure can be retained as metastable phases at atmospheric pressure by cooling them to 77°K before the high pressure is removed. Resistivity measurements made as the temperature slowly increases above 77°K have been used to study the temperature dependence of the rates at which InSb_{II} and the solid solutions are transformed into the zincblende phase (InSb_{I}) stable at atmospheric pressure and into two-phase mixtures of InSb_{I} and tin, respectively. Rapid transformation occurs for InSb at about 200°K and for the solid solutions at higher temperatures, which increase with increasing tin content.

The room temperature resistance R of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ samples with x between 0 and 0.20 has been measured as a function of pressure up to 70 kbar. For HgTe , R increases abruptly by four orders of magnitude at about 15 kbar due to a phase transformation from zincblende to einnabar structure. Similar but smaller increases are observed at somewhat higher pressures in the samples containing cadmium, presumably because of the same transformation. Below the transformation pressure, there are significant changes in R which are probably due primarily to the effect of pressure on the band structure.

The partial pressures of Cd(g) and $\text{Te}_2(\text{g})$ in equilibrium with congruently subliming CdTe(e) between 780° and 939°C have been determined by measuring the optical density of the vapor between 2000 and 6000 Å with a double-beam spectrophotometer. The partial pressures are given by $\log p_{\text{Te}_2} (\text{atmospheres}) = -(1.00 \times 10^4)/T + 6.346$ and $p_{\text{Cd}} = 2p_{\text{Te}_2}$. The expression for the Gibbs free energy of formation calculated from these equations is in good agreement with the results of electrochemical and effusion experiments at lower temperatures.

Manganese in MnO and cobalt in CoO have been determined by automatic potentiometric EDTA titrations. Automatic titration methods are being developed for the determination of indium, antimony, and tellurium in samples containing these three elements as the major

constituents. Satisfactory results have been obtained so far in analyses on samples weighing 0.5 gram or more.

IV. BAND STRUCTURE AND SPECTROSCOPY OF SOLIDS

Several new observations have been made in the magnetospectroscopic investigations of various materials. Reststrahlen reflection has been observed from the surface of HgTe at low temperatures. From these data one obtains values for the lattice absorption frequency, the high-frequency dielectric constant, and the effective charge which are $\nu_o = 3.45 \times 10^{12}$, $\epsilon_o = 14$, and $q^* = 0.6e$, respectively. The data also show a broad absorption band in the same region which may be due to an interband transition.

The magneto-optical reflectivity data from another semimetal, antimony, has also proved interesting. Two types of magnetic behavior were observed: (1) a large magnetoplasma effect and (2) an oscillatory term in the reflectivity, smaller in magnitude than the magnetoplasma effect, but in the same photon energy region. The oscillatory term, which arises from the deHaas-Shubnikov mechanism, leads to results in good agreement with other determinations of the periods along the single-crystal axes. The features of the oscillatory term can be understood on the basis of a simple parabolic conduction band. It is believed that this effect has not previously been observed experimentally.

The indirect transition in germanium has been re-examined using improved measurement techniques, higher magnetic fields and the Faraday configuration. Magneto-absorption data as a function of wavelength show transitions from the valence band edge to the electronic Landau ladders in the conduction band. Superimposed on these large intensity effects is a fine structure due to hole ladders in the valence band. In addition, a spin splitting in the conduction band was observed corresponding to electronic g -factors of 1.8 and 1.5 in the [100] and [110] orientations, respectively. These are in agreement with the theoretical predictions. The Zeeman splitting of the indirect exciton was also observed for various orientations. This effect has been measured in magnetic fields sufficiently high (at the National Magnet Laboratory, M.I.T.) so that the magnetic energy is much greater than the electric energy of the exciton, and a linear behavior is observed. It will be necessary to extend the theory to the high-magnetic-field region to compare with the experimental data.

Measurements in the ultraviolet of the reflectivity of Mg_2Ge show spectral structure in the region between 2.5 and 11 eV. Since the available band structure calculation is limited in accuracy, positive identification of the spectral peaks is not possible at present. It is expected that measurements on Mg_2Si will make identification easier.

Galvanomagnetic measurements on HgTe have been initiated. Rotational measurements of the magnetoresistance, with magnetic field perpendicular to the current, indicated little if any anisotropy. In measurements of the magnetic field dependence of the magnetoresistance and Hall effects, several interesting effects were observed which are incompatible with a one-band model of the material. However, the experimental results are consistent with mixed electron and hole conduction. The data are additional evidence for the semimetal band model of HgTe. Measurements and calculations are being continued.

A general theory for the Seebeck coefficient tensor in a magnetic field has been developed in terms of symmetry properties. Tables providing easy access to the results of the theory including the spatial symmetry properties are being prepared. These results have been useful in understanding the galvano-thermomagnetic properties of bismuth.

V. MAGNETISM AND RESONANCE

Our present program includes work on three classes of electrons found in solids: broad-band electrons, narrow-band electrons, and localized electrons.

Experimental studies on narrow-band electrons have been hindered by a failure to know what type of material to study. We have shown that there are three classes of transition-metal compounds whose physical properties are dominated by narrow-band electrons, and that all three classes can be found among transition-metal oxides. Primarily ionic compounds which have a cation-cation separation so small that a cation-sublattice d-band is formed are illustrated by high-temperature VO or V_2O_3 . Covalent compounds having partially filled π^* bands are illustrated by the bronzes Na_xWO_3 or by metallic ReO_3 . Covalent compounds having partially filled σ^* bands are illustrated by metallic $LaNiO_3$. High-temperature VO_2 contains electrons in overlapping cation-sublattice and π^* bands. In order to demonstrate the validity of this explanation of the metallic properties of Na_xWO_3 as against the two proposals extant in the literature, pure ReO_3 and ordered $SrMg_{0.5}Re_{0.5}O_3$ have been prepared and shown to be metallic and semiconducting, respectively.

In order to study the transport properties of the vanadium spinels, which illustrate primarily ionic compounds having a cation-cation separation near the critical separation for collective-electron vs localized-electron behavior, a method has been developed for the preparation of single crystals of controlled chemistry.

The band structure of PbSe is being investigated by cyclotron resonance. A resonance has been observed in p-type material at 70 Gcps and 4.2°K.

A theoretical study of the six-membered hydrogen ring has led to a one-parameter formulation of the electronic wave functions that reduces, for one limit of the parameter, to the molecular-orbital formalism applicable at very small internuclear distances and, for the other limit, to atomic Wannier orbitals with near-neighbor spins correlated antiparallel, which is the correct boundary condition for large separations. A high degree of symmetry makes calculation relatively simple, and the calculated binding energies were better for all separations than those obtained by an alternant-molecular-orbital calculation. The method can be extended to three-dimensional lattices containing two sublattices.

The complex spin configurations of the rare-earth metals can be derived from a Hamiltonian that includes a Ruderman-Kittel exchange interaction and magnetic anisotropy. Exchange striction has been added to the Hamiltonian, and it is shown that below the Curie temperature there should be an observable sinusoidal variation in the c-axis spacing of the linear and the high-temperature magnetic phase of erbium.

Spin-wave resonance provides an important check on the theory of magnetic exchange interactions. In order to examine some new exchange effects and to obtain the greater accuracy that will be required, this technique has been extended from 10 to 70 Gcps.

Magnetic susceptibility of the compound $\text{MnAs}_{0.9}\text{P}_{0.1}$ indicates that with decreasing temperature there is spin quenching over the 120 °C temperature interval below the $\text{B31} \leftrightarrow \text{B8}_1$ transition temperature.

The Jahn-Teller Mn^{3+} ion has been shown to be unique in its destruction of long-range ionic ordering in $\text{Li}_{0.5}\text{M}_{2.5}^{3+}\text{O}_3$ spinels.

Spin-resonance observations in CoCr_2O_4 have been extended to 315 Gcps. The spectrum as a function of temperature shows a behavior that extrapolates smoothly from lower frequency data. Although CoCr_2O_4 and MnCr_2O_4 have complex-spiral spin configurations, neutron diffraction and high-field studies reveal that MnCr_2S_4 has a collinear Néel configuration with a $\mu_{\text{Mn}} = 4.7\mu_{\text{B}}$, rather than a spin-only $5\mu_{\text{B}}$ and a Cr-Cr interaction that is ferromagnetic rather than antiferromagnetic.

A calculation of the first-order effect of spin-orbit coupling on a $3d^5$ unperturbed S-state ion in a cubic crystal field has given a new anisotropy contribution to the spin density. In $\alpha - \text{Fe}_2\text{O}_3$, this new term is the same order of magnitude as the spherical Dzialoshinsky term that contributes to the parasitic ferromagnetism. This term plus the Dzialoshinsky term can account for the highly aspherical ferromagnetic spin-density distribution found in recent neutron-diffraction work.

The temperature dependence of attenuation of 70-Gcps phonons in quartz has been determined. Attenuation measurements, made chiefly on the first echo, have led to a fourth-power dependence with temperature.

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13. ABSTRACT

This abbreviated report covers the work of Division 8 from April 1964 through 30 June 1964. A more detailed presentation is covered by the Solid State Research Report for the same period.

14.

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